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Specific Generation of Lithiated 3-Trimethylsiloxy-1,2-propadiene Derivatives from 1-(Trimethylsilyl)propargyl Alcohols

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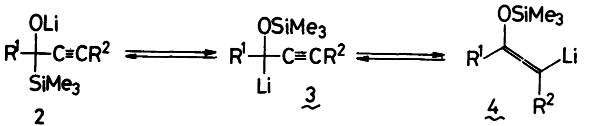
1-(Trimethylsilyl)propargyl alcohols have been prepared by treating acyltrimethylsilanes with magnesium acetylides, and their base-induced reactions involving rearrangement of silyl group have been examined. Treatment of the alcohol with an equimolar amount of butyllithium in hexane followed by addition of tetrahydrofuran has allowed to generate the lithiated 3-trimethylsiloxy-1,2-propadiene, which reacts with an alkyl iodide to afford the alkylated 1-trimethylsiloxy-1,2-propadiene in high yield. Further, a catalytic amount of butyllithium also effects an efficient conversion of the alcohol to the corresponding 1-siloxy-1,2-propadiene through a similar rearrangement process.

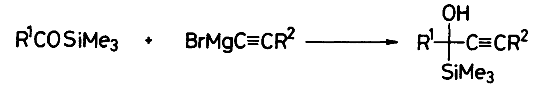
Strong affinity of silicon atom to oxide anion has sometimes allowed a facile transfer of trialkylsilyl group from carbon to oxygen. Under basic conditions, 1-(trialkylsilyl)alkanols undergo rearrangement to yield the corresponding alkyl silyl ethers, which is well documented as Brook rearrangement.[1,2] Similar migration of silyl group has also been proposed for Peterson type olefination reaction[2] of 2-(trialkylsilyl)-alkanols under basic conditions.[3] In these rearrangement processes, formation of the corresponding carbanionic species during equilibration with the alkoxides has been assumed or proved in certain cases, but it has been quite difficult to make use such kinds of nucleophilic species for carbon chain homologation because of their high lability under reaction conditions. To control a generation of such carbanionic species effectively through this rearrangement, an additional anion-stabilizing substituent such as phenyl or olefinic group seems to be required, and we have recently reported several synthetic applications of such anionic species generated from 1-(trimethylsilyl)-allylic alcohols[4] and 3-trimethylsilyl-4-penten-1-ol derivative[5] for synthesis of enol silyl ethers and 1,5-heptadien-3-ol, an oxy-Cope rearrangement precursor.

Based on a similar background, 1-(trimethylsilyl)-propargyl alcohols (**1**) have also been expected to undergo silyl group migration to generate anionic species of propargyl silyl ether **3** or 1-trimethylsiloxy-1,2-propadiene derivatives **4** under basic conditions. Different from the precedent cases, an internal coordination of siloxy group to metal which has brought about a thermodynamic stability may be ruled out from these anionic species **3** and **4**, but allenic species **4** is expected to be much more common than **3** judging from literatures dealing with metallated allene derivatives.[6] Resulting nucleophiles **4** seem to be especially useful on synthetic standpoints that selective introduction of various organic substituents may be feasible on both α- and β-carbons of α,β-unsaturated carbonyl compounds (Scheme 1). In this paper we describe full details on the rearrangement reactions of the propargyl alcohol **1** to afford siloxy allenes **5** and **6**.[7,8]



Scheme 1.

The starting materials, 1-(trimethylsilyl)propargyl alcohols (**1**) were easily prepared by treating the corresponding acyltrimethylsilanes[9] with appropriate bromomagnesium acetylides (Eq. 1). A straight-chained acyltrimethylsilane undergoes addition of acetylides quite efficiently in ether to give the corresponding **1** as a sole product, whereas a small amount of rearrangement prouct, propargyl silyl ether, is also formed from the addition reaction of an α-branched acyltrimethylsilane when ether or tetrahydrofuran (THF) is employed as the solvent. In the latter case, use of hexane as the reaction solvent excludes the formation of side-product, and the desired **1** could be obtained in high yield.



$$R^1COSiMe_3 + BrMgC\equiv CR^2 \longrightarrow R^1-\underset{SiMe_3}{\overset{OH}{C}}-C\equiv CR^2 \qquad (1)$$

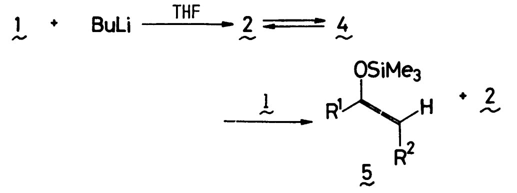
1

Table 1. Preparation of 1-(trimethylsilyl)-propargyl alcohols (**1**)

	R^1	R^2	Yield/% of **1**
a)	C_3H_7	C_6H_5	96
b)	$C_6H_5CH_2CH_2$	C_4H_9	95
c)	$C_6H_5CH_2CH_2$	C_6H_5	99
d)	$C_6H_5CH_2CH_2$	$SiMe_3$	96
e)	$C_6H_5CH_2CH_2$	CH_2OCH_3	94

On lithiation of this alcohol **1** with butyllithium, we have experienced similar difficulties encountered with 1-(trimethylsilyl)allylic alcohols:[4] complete conversion of the alcohol **1** to the lithium alkoxide **2** is quite difficult when tetrahydrofuran is used as the solvent. Formation of complex mixture has usually been observed on treatment of the resulting solution with various electrophiles. This curious result may be explained by assuming that an extremely rapid equilibrium between the lithium alkoxide **2** and the lithiated allenic species **4** has been attained through rearrangement of silyl group from carbon to oxygen before complete formation of **2**. The resulting carbanionic species **4** may be protonated by the remaining alcohol **1**, which leads to fomation of a mixture of siloxyallene **5** and its lithiated one **4** together with the alkoxide **2** and butyllithium (Eq. 2).

However, use of a nonpolar solvent such as hexane has excluded the equilibration between **2** and **4**, and the alcohol **1** can be converted to the corresponding lithium alkoxide **3** almost completely. Further, addition of


(2)

THF to the resulting hexane solution induces the equilibration to generate **4**. Carbon chain homologation can be achieved efficiently by the *in situ* reaction of this species with appropriate alkyl halides. Although two types of alkylation products may be conceivable during this procedure, the reaction takes place selectively on allenic carbon as expectedly,[6] and the corresponding α,β-unsaturated ketone **7** is obtained in high yield after aqueous work-up of the reaction mixture (see Scheme 2 and Table 2). Only exceptional case is that bearing a leaving group on an appropriate position, which undergoes a facile elimination as shown in the following example.

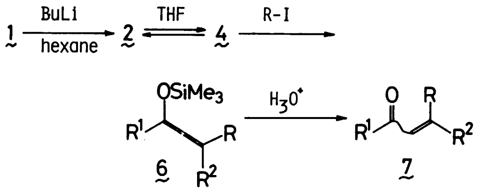
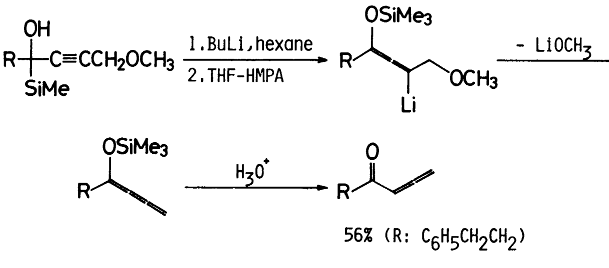
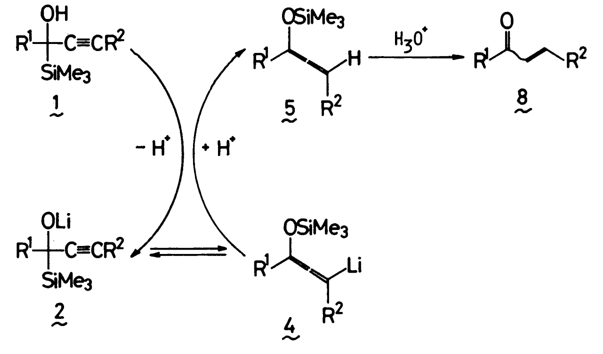

Scheme 2.

Table 2. Alkylation of lithiated allenes **4**

	R^1	R^2	R-I	Yield/% of **7**
a)	C_3H_7	C_6H_5	CH_3-I	92
b)	$C_6H_5CH_2CH_2$	C_4H_9	CH_3-I	94
c)	$C_6H_5CH_2CH_2$	C_6H_5	CH_3-I	92
d)	$C_6H_5CH_2CH_2$	C_6H_5	C_4H_9-I	86
e)	$C_6H_5CH_2CH_2$	$SiMe_3$	CH_3-I	87
f)	$C_6H_5CH_2CH_2$	$(C_2H_4O_2)$-$CHCH_2CH_2$	CH_3-I	82


(3)

Further, in a similar manner with 1-(trimethylsilyl)-allylic alcohols,[4] the alcohols **1** undergo a specific conversion to the corresponding 1-trimethylsiloxy-1,2-propadienes in excellent yield under the influence of a catalytic amount of butyllithium in THF through the following four steps: (1) formation of the alkoxide **2**, (2) generation of lithiated allenic species **4** *via* equilibration, (3) protonation of **4** with the remaining alcohol, and (4) regeneration of the alkoxide **2**. This transformation has been effected by treating the alcohol **1** with *ca.* 5 mol% of butyllithium in THF at −78 °C followed by warming up to 0 °C.


Scheme 3.

In most cases, protonation takes place selectively on terminal allenic carbon to yield **5**, but the alcohol prepared from silylacetylene afforded a mixture of the corresponding **5** (63%) and the propargyl silyl ether (29%).

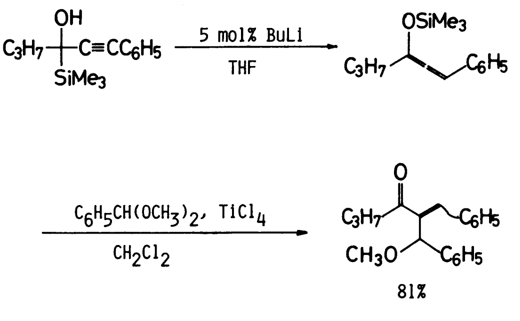
Unfortunately, on an attempt for purification, the resulting siloxyallenes **5** and **6** are very labile on column chromatography and sometimes on heating for a distillation. Accordingly, the yields of the products were determined on the basis of α,β-unsaturated ketones **8** obtained by aqueous work-up of the reaction mixture. The results are shown in Table 3.

Table 3. Catalytic conversion of alcohols **1** to **8** *via* **5**

	R^1	R^2	Yield/% of **8**
a)	C_3H_7	C_6H_5	96
b)	$C_6H_5CH_2CH_2$	C_4H_9	97
c)	$C_6H_5CH_2CH_2$	C_6H_5	89
d)	$C_6H_5CH_2CH_2$	$SiMe_3$	63[a]
e)	$C_6H_5CH_2CH_2$	CH_2OCH_3	80

[a] The propargyl silyl ether was also formed in 29% yield.

However, the crude products **5** are usually pure enough for further synthetic elaboration without purification. By using the crude 5, several organic substituents can be introduced on the central carbon of the allenic linkages very efficiently under the influence of Lewis acid as shown below. For example, the crude **5** (R^1=C_3H_7, R^2=C_6H_5) obtained from the corresponding alcohol **1** gave the condensation product in 81% overall yield on treating with a benzaldehyde acetal. Thus, starting from the alcohol **1**, this procedure has allowed to effect two types of carbon chain homologation on each α- and β-carbon, respectively, by way of lithiated allenic species **4**.


(4)

Experimental

General Methods. Boiling points are uncorrected. Infrared (IR) spectra were recorded on a Hitachi EPI-G3 spectrometer; absorptions are reported in reciprocal centimeters. Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a Hitachi R-24B spectrometer; chemical Shifts (δ) are expressed in part per million downfield from tetramethylsilane. Analytical gas-liquid chromatography (GLC) was performed on a Hitachi 163 instrument with a flame-ionization detector and nitrogen carrier gas (1.0—1.3 kg/cm^2) using a OV-101 fused silica 20 m capillary column (Hitachi Chemi-Column). Microanalysis were performed with a Perkin-Elmer 240 at the Microanalytical Laboratory, Tokyo Institute of Technology.

Reactions involving air- or moisture-sensitive compounds were carried out in appropriate round-bottomed flasks with stirring bars under nitrogen or argon. Bulb-to-bulb distillation was performed with a Buchi Kugelrohr apparatus.

Preparative thin-layer chromatography (TLC) was carried out on glass plates (20 × 20 cm) coated with Merck silica gel PF 254 (1 mm thick).

Hexane was distilled from sodium. Ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl immediately before use.

Materials. Acyltrimethylsilanes were prepared from the corresponding enol trimethylsilyl ethers of benzene- or methane-thiol esters according to the procedure developed in our laboratory.[9]

*Preparation of 1-(Trimethylsilyl)propargyl Alcohols (***1***).* *General Procedure*: To ethylmagnesium bromide (32 mL of 0.71 M THF solution, 22.5 mmol) diluted with ether (50 mL) was added an ethereal solution (25 mL) of a substituted acetylene (25 mmol) at 0 °C and it kept stirring for 30 min at room temperature. Then, an acyltrimethylsilane (15 mmol) in ether (25 mL) was added to the resulting solution and was stirred further 10 min at 0 °C. The reaction mixture was quenched with satd aq NH_4Cl and was extracted three times with 50 mL portions of ether. The extracts were washed with satd aq NaCl and were dried over anhyd $MgSO_4$. Removal of the solvent from the filtrate followed by distillaion gave the corresponding 1-(trimethylsilyl)propargyl alcohol (**1**).

1-Phenyl-3-trimethylsilyl-1-hexyn-3-ol (1a): Bp 101—102 °C/0.05 mmHg;[10] IR (neat) 3400, 2200, 1245, 840 cm^{-1}; NMR (CCl_4) δ=0.16 (s, 9H), 0.80—1.20 (m, 3H), 1.43—1.87 (m, 5H including a singlet of OH at 1.73), 7.03—7.43 (m, 5H); Calcd for $C_{15}H_{22}OSi$: C, 73.10; H, 9.02%. Found: C, 73.21; H, 8.94%.

1-Phenyl-3-trimethylsilyl-4-nonyn-3-ol (1b): Bp 118—119 °C/0.025 mmHg; IR (neat) 3430, 1600, 1250, 845 cm^{-1}; NMR (CCl_4) δ=0.12 (s, 9H), 0.73—2.03 (m, 10H including a singlet of OH at 1.55), 2.06—2.47 (m, 2H), 2.67—3.05 (m, 2H), 7.13 (s, 5H); Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78%. Found: C, 74.81; H, 9.79%.

1,5-Diphenyl-3-trimethylsilyl-1-pentyn-3-ol (1c): Bp 146—147 °C/0.037 mmHg; IR (neat) 3410, 1600, 1250, 850 cm^{-1}; NMR (CCl_4) δ=0.18 (s, 9H), 1.76—2.16 (m, 3H including a singlet of OH at 1.91), 2.75—3.16 (m, 2H), 7.00—7.50 (m, 10H).

5-Phenyl-1,3-bis(trimethylsilyl)-1-pentyn-3-ol (1d): Bp 104—105 °C/0.025 mmHg; IR (neat) 3400, 2135, 1248, 845 cm^{-1}; NMR (CCl_4) δ=0.12 (s, 9H), 0.19 (s, 9H), 1.62—2.03 (m, 3H including a singlet of OH at 1.67), 2.68—3.03 (m, 2H), 7.16 (s, 5H); Calcd for $C_{17}H_{28}OSi_2$: C, 67.04; H, 9.27%. Found: C, 67.32; H, 9.22%.

6-Methoxy-1-phenyl-3-trimethylsilyl-4-hexyn-3-ol (1e): Bp 110—112 °C/0.027 mmHg; IR (neat) 3370, 2200, 1246, 840 cm^{-1}; NMR (CCl_4) δ=0.15 (s, 9H), 1.65—2.08 (m, 2H), 2.37 (s, 1H), 2.68—3.10 (m, 2H), 3.31 (s, 3H), 4.12 (s, 2H), 7.13 (s, 5H); Calcd for $C_{16}H_{24}OSi$: C, 69.52; H, 8.75%. Found: C, 69.20; H, 8.60%.

Alkylation of a Lithiated Allene 4 Generated from **2**. *General Procedure*: To a hexane (1 mL) solution of 1-(trimethylsilyl)propargyl alcohol (**1**) (1 mmol) was added butyllithium (0.55 mL of 2.0 M hexane solution, 1.1 mmol) at 0 °C and it was stirred for 30 min. After cooling to −78 °C, THF (5 mL) was added and it was stirred for 10 min at that temperature. Then, an appropriate alkyl iodide (1.2 mmol) in THF (1 mL) was added and the reaction mixture was stirred for 1.5 hr at −40 °C. Hexane (20 mL) precooled to −78 °C was added to the reaction mixture and was poured into a buffer (KH_2PO_4–NaOH) solution. The aqueous layer was extracted twice with 20 mL portions of ether, and the combined extracts were dried over anhyd $MgSO_4$. After removal of the solvent, the crude 1-(trimethylsiloxy)allene (**6**) was dissolved in THF (10 mL) and 3—5 drops of 1M HCl was added. After stirring for 20 min at room temperature, the reaction mixture was treated with aq $NaHCO_3$ and was extracted twice with 20 mL portions of ether. The combined extracts were washed with satd aq NaCl and dried over anhyd $MgSO_4$. Removal of the solvent followed by separation with TLC gave a mixture of the corresponding (*E*)- and (*Z*)-α,β-unsaturated ketone.

5-Methyl-1-phenyl-3-trimethylsiloxy-3,4-nonadiene (6a): IR (neat) 1950, 1600, 1250, 850 cm^{-1}; NMR (CCl_4) δ=0.12 (s, 9H), 0.70—2.93 (m, 16H), 7.10 (s, 5H).

2,6-Diphenyl-4-trimethylsiloxy-2,3-hexadiene (6c): IR (neat) 1934, 1600, 1250, 845 cm^{-1}; NMR (CCl_4) δ=0.10 (s, 9H), 2.00 (s, 3H), 2.30—3.00 (m, 4H), 7.12 (s, 10H).

(E)-*2-Phenyl-2-hepten-4-one (7a-(***E***))*: 16%; IR (neat) 1675, 1595 cm^{-1}; NMR (CCl_4) δ=0.95 (t, *J*=7 Hz, 3H), 1.33—1.93 (m, 2H), 2.43 (t, *J*=7 Hz, 2H), 2.50 (s, 3H), 6.36 (s, 1H), 7.03—7.63 (m, 5H).

(Z)-*2-Phenyl-2-hepten-4-one (7a-(***Z***))*: 76%; IR (neat) 1685, 1655, 1610 cm^{-1}; NMR (CCl_4) δ=0.70 (t, *J*=6 Hz, 3H), 1.03—1.70 (m, 2H), 1.98 (t, *J*=6 Hz, 2H), 2.11 (s, 3H), 5.99 (s, 1H), 7.00—7.40 (m, 5H).

(E)-*5-Methyl-1-phenyl-4-nonen-3-one (7b-(E))*: 45%; IR (neat) 1676, 1609 cm^{-1}; NMR (CCl_4) δ=0.66—1.67 (m, 7H), 1.76—2.30 (m, 2H), 2.04 (d, *J*=1 Hz, 3H), 2.40—3.02 (m, 4H), 5.87 (q, *J*=1 Hz, 1H), 7.04 (s, 5H).

(Z)-*5-Methyl-1-phenyl-4-nonen-3-one (7b-(***Z***))*: 49%; IR (neat) 1679, 1606 cm^{-1}; NMR (CCl_4) δ=0.68—1.57 (m, 7H), 1.78 (d, *J*=1 Hz, 3H), 2.34—3.01 (m, 6H), 5.85 (q, *J*=1 Hz, 1H), 7.01 (s, 5H).

(E)-*1,5-Diphenyl-4-hexen-3-one (7c-(E))*: 28%; IR (neat) 1680, 1600 cm^{-1}; NMR (CCl_4) δ=2.48 (d, *J*=1.6 Hz, 3H), 2.60—3.06 (m, 4H), 6.32 (q, *J*=1.6 Hz, 1H), 6.97—7.45 (m, 10H).

(Z)-*1,5-Diphenyl-4-hexen-3-one (7c-(***Z***))*: 64%; IR (neat) 1685, 1655, 1610 cm^{-1}; NMR (CCl_4) δ=2.13 (d, *J*=1.4 Hz, 3H), 2.13—2.87 (m, 4H), 5.96 (q, *J*=1.4 Hz, 1H), 6.65—7.47 (m, 10H).

(E)-*1,5-Diphenyl-4-nonen-3-one (7d-(E))*: 17%; IR (neat) 1668, 1585 cm^{-1}; NMR (CCl_4) δ=0.73—1.57 (m, 7H), 2.67—3.17 (m, 6H), 6.22 (s, 1H), 7.10 (s, 5H).

(Z)-*1,5-Diphenyl-4-nonen-3-one (7d-(Z))*: 69%; IR (neat) 1680, 1650, 1605 cm^{-1}; NMR (CCl_4) δ=0.70—1.57 (m, 7H), 2.07—2.87 (m, 6H), 5.95 (s, 1H), 6.70—7.37 (m, 10H).

(E)-*1-Phenyl-5-trimethylsilyl-4-hexen-3-one (7e-(E))*: 39%; IR (neat) 1675, 1578, 1250, 850 cm^{-1}; NMR (CCl_4) δ=0.11 (s, 9H), 2.12 (d, *J*=2 Hz, 3H), 2.60—2.98 (m, 4H), 6.25 (q, *J*=2 Hz, 1H), 7.09 (s, 5H).

(Z)-*1-Phenyl-5-trimethylsilyl-4-hexen-3-one (7e-(***Z***))*: 48%; IR (neat) 1675, 1570, 1242, 850 cm^{-1}; NMR (CCl_4) δ=0.13 (s, 9H), 1.93 (d, *J*=1.8 Hz, 3H), 2.60—2.94 (m, 4H), 6.56 (q, *J*=1.8 Hz, 1H), 7.10 (s, 5H).

(E)-*and* (Z)-*4-Methyl-6-oxo-8-phenyl-4-octenal Ethylene Acetal (7f)*: 82%; IR (neat) 1678, 1610 cm^{-1}; NMR (CCl_4) δ=1.47—3.03 (m, 11H), 3.60—3.91 (m, 4H), 4.71 and 4.78 (t, J=4 Hz, 1H), 5.94 (q, J=1 Hz, 1H), 7.08 (s, 5H).

1-Phenyl-4,5-hexadien-3-one. To a THF (6 mL) solution of 6-methoxy-1-phenyl-3-trimethylsilyl-4-hexyn-3-ol (276 mg, 1.0 mmol) was added butyllithium (0.67 mL of 1.5 M hexane solution, 1.0 mmol) and hexamethylphosphoric triamide (HMPA) successively at −78 °C, and it was stirred for 2 h at −40 °C. Then, the reaction mixture was worked up in a similar manner as described above to afford the title compound (96 mg, 56%). Bp 90—92 °C/0.08 mmHg; IR (neat) 1940, 1915, 1665, 855 cm^{-1}; NMR (CCl_4) δ=2.80 (s, 4H), 5.70 (d, J=6 Hz, 2H), 5.65 (dd, J=6 and 6 Hz, 1H), 7.08 (s, 5H); Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.89; H, 7.10%.

Conversion of 1-(Trimethylsilyl)propargyl Alcohol (1) to the 1-Trimethylsiloxy-1,2-propadiene (5) Catalyzed by Butyllithium. General Procedure: Buytllithium (0.04 mL of 1.5 M hexane solution, 0.06 mmol) was added to a THF (5 mL) solution of a 1-(trimethylsilyl)propargyl alcohol (**1**) (1 mmol) at −78 °C, and the reaction mixture was warmed up to 0 °C during 1 h. After stirring for 20 min at that temperature, the reaction mixture was worked up in a similar manner as described above to give the corresponding **8**.

1-Phenyl-3-trimethylsiloxy-1,2-hexadiene (5a): Bp 88—89 °C/0.035 mmHg; IR (neat) 1925, 1250, 850 cm^{-1}; NMR (CCl_4) δ=0.13 (s, 9H), 0.94 (t, J=7 Hz, 3H), 1.71—1.81 (m, 2H), 2.17 (dt, J=7 and 2 Hz, 2H), 6.38 (t, J=2 Hz, 1H), 7.16 (s, 5H).

1,5-Diphenyl-3-trimethylsiloxy-1,2-pentadiene (5c): IR (neat) 1930, 1250, 850 cm^{-1}; NMR (CCl_4) δ=0.14 (s, 9H), 2.40—3.00 (m, 4H), 6.37 (t, J=2 Hz, 1H), 6.90—7.37 (m, 10H).

(E)-*1-Phenyl-1-hexen-3-one (8a-(E))*: 24%; IR (neat) 1675, 1650, 1600 cm^{-1}; NMR (CCl_4) δ=0.95 (t, J=7 Hz, 3H), 1.68 (tq, J=7 and 7 Hz, 2H), 2.55 (t, J=7 Hz, 2H), 6.58 (d, J=16 Hz, 1H), 7.41 (d, J=16 Hz, 1H), 7.15—7.55 (m, 5H).

(Z)-*1-Phenyl-1-hexen-3-one (8a-(Z))*: 72%; IR (neat) 1675, 1590 cm^{-1}; NMR (CCl_4) δ=0.85 (t, J=7 Hz, 3H), 1.56 (tq, J=7 and 7 Hz, 2H), 2.31 (t, J=7 Hz, 2H), 6.01 (d, J=12 Hz, 1H), 6.65 (d, J=12 Hz, 1H), 7.08—7.65 (m, 5H).

(E)-*1-Phenyl-4-nonen-3-one (8b-(E))*: 75%; IR (neat) 1685, 1665, 1620 cm^{-1}; NMR (CCl_4) δ=0.71—1.62 (m, 7H), 1.88—2.38 (m, 2H), 2.63—2.95 (m, 4H), 5.95 (dq, J=16 and 1 Hz, 1H), 6.68 (dt, J=16 and 6 Hz, 1H), 7.09 (s, 5H).

(Z)-*1-Phenyl-4-nonen-3-one (8b-(Z))*: 22%; IR (neat) 1682, 1610 cm^{-1}; NMR (CCl_4) δ=0.68—1.61 (m, 7H), 2.42—3.05 (m, 6H), 5.83—6.12 (m, 2H), 7.10 (s, 5H).

(E)-*1,5-Diphenyl-1-penten-3-one (8c-(E))*: 43%; IR (neat) 1680, 1650, 1600 cm^{-1}; NMR (CCl_4) δ=2.89 (s, 4H), 6.56 (d, J=16 Hz, 1H), 7.41 (d, J=16 Hz, 1H), 6.97—7.50 (m, 10H).

(Z)-*1,5-Diphenyl-1-penten-3-one (8c-(Z))*: 46%; IR (neat) 1678, 1595; NMR (CCl_4) δ=2.40—2.97 (m, 4H), 5.97 (d, J=12 Hz, 1H), 6.63 (d, J=12 Hz, 1H), 6.87—7.60 (m, 10H).

(E)-*5-Phenyl-1-trimethylsilyl-1-penten-3-one (8d-(E))*: 52%; IR (neat) 1670, 1249, 842 cm^{-1}; NMR (CCl_4) δ=0.10 (s, 9H), 2.79 (s, 4H), 6.29 (d, J=19 Hz, 1H), 6.91 (d, J=19 Hz, 1H), 7.05 (s, 5H).

(Z)-*5-Phenyl-1-trimethylsilyl-1-penten-3-one (8d-(Z))*: 11%; IR (neat) 1680, 1240, 845 cm^{-1}; NMR (CCl_4) δ=0.11 (s, 9H), 2.67—2.93 (m, 4H), 6.17 (d, J=14 Hz, 1H), 6.70 (d, J=14 Hz, 1H), 7.02 (s, 5H).

(E)-*6-Methoxy-1-phenyl-4-hexen-3-one (8e-(E))*: 53%; IR (neat) 1680, 1660, 1625 cm^{-1}; NMR (CCl_4) δ=2.79 (s, 4H), 3.27 (s, 3H), 3.93 (dd, J=4 and 1.8 Hz, 1H), 6.16 (dt, J=16 and 1.8 Hz, 1H), 6.67 (dt, J=16 and 4 Hz, 1H). 7.11 (s, 5H).

(Z)-*6-Methoxy-1-phenyl-4-hexen-3-one (8e-(Z))*: 27%; IR (neat) 1680, 1610 cm^{-1}; NMR (CCl_4) δ=2.63—2.90 (m, 4H), 3.28 (s, 3H), 4.35 (d, J=2 Hz, 2H), 6.00—6.18 (m, 2H), 7.10 (s, 5H).

The Reaction of 1-Phenyl-3-trimethylsiloxy-1,2-hexadiene with Benzaldehyde Dimethyl Acetal. 1-Phenyl-3-trimethylsiloxy-1,2-hexadiene was prepared from 1-phenyl-3-trimethylsilyl-1-hexyn-3-ol (246 mg, 1.0 mmol) by procedures described above. The crude diene was dissolved in dichloromethane (4 mL) and was added to a mixture of benzaldehyde dimethyl acetal (152 mg, 1.0 mmol) and titanium tetrachloride (0.11 mL, 1.0 mmol) in dichloromethane (8 mL) at −78 °C. After stirring for 1 h at that temperature, the reaction mixture was poured into 0.4 M aq $NaHCO_3$ (20 mL) and was filtered through Celite. The aqueous layer was extracted twice with 20 mL portions of dichloromethane, and the combined extracts were dried over anhyd $MgSO_4$. Removal of the solvent from the filtrate followed by separation with TLC afforded 2-(α-methoxybenzyl)-1-phenyl-1-hexen-3-one (237 mg, 81% based on 1-phenyl-3-trimethylsilyl-1-hexyn-3-ol). Bp 118—119 °C/0.024 mmHg; IR (neat) 1680 cm^{-1}; NMR (CCl_4) δ=0.61 (t, J=8 Hz, 3H), 0.91—2.35 (m, 4H), 5.00 (s, 1H), 6.43 and 6.45 (s, 1H), 7.07 (s, 5H), 7.21 (s, 5H); Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53%. Found: C, 81.84; H, 7.58%.

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10) 1 mmHg=133.322 Pa.